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DETERMINATION OF SULFURIC ACID IN ANODIZING AND HARDCOATING SOLUTIONS BY ACID-BASE TITRATION USING A pH METER

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The chemical literature lacks an acceptable analytical method for adequately monitoring sulfuric acid in aluminum finishing solutions during the finishing processes. These solutions include anodizing and hardcoating solutions. In this report, an improved method is presented that provides acceptable analysis and monitoring of this acid during the finishing processes. The optimum operating ranges of this acid are 90 to 150 g/l and 120 to 150 g/l for the respective anodizing and hardcoating solutions. The resulting precisions are

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in the range of 1 to 3 g/l, providing adequate monitoring of these metal finishing solutions supported by seven years of testing.

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INTRODUCTION

The chemical literature lacks an acceptable analytical method for adequately monitoring sulfuric acid in aluminum finishing solutions during the anodizing and hardcoating processes. Lack of optimization of these finishing solutions causes serious problems for the aluminum finishing industry such as poor quality products and wasted resources.

An analytical method to determine sulfuric acid in these solutions is a sodium hydroxide titrant and a phenolphthalein indicator to detect the endpoint for this acid (ref 1). The problem associated with this method is that the color changes at the endpoint for these sample solutions are gradual and indistinct. This is shown in the literature in the acid-base titration chapter of Fritz and Schenk (ref 2), where the endpoint with this indicator varies by plus or minus one pH unit depending on the chemistry of the solution. Relative precisions of this method are in the range of 2 to 4 percent.

Another chemical analysis method to determine sulfuric acid in these solutions is a sodium hydroxide titrant where a titration curve is acquired for the sample solution. This method is not given anywhere in the literature, but it can be derived from basic principles (refs 2,3). The inflection point or first derivative of the titration curve provides the endpoint of the acid titration. The problem associated with this method is that acquiring titration curves is a time-consuming and tedious procedure which is unacceptably slow for this application. Automated titrators were used to make the procedure less time-consuming and less tedious, but they do not locate the endpoints precisely for sulfuric acid as experienced by this author. Relative precisions of this method are in the range of 2 to 3 percent.

References are listed at the end of this report.

The theoretical endpoint and pH value to determine sulfuric acid in the finishing solutions by a sodium hydroxide titrant can be calculated to 0.1 pH unit from the data in the acid-base titration chapters of Fritz and Schenk (ref 2) and Peters et al. (ref 3) for these chemical conditions.

The simple method presented in this report provides acceptable analysis and monitoring of this acid in the finishing solutions. The method uses the sodium hydroxide titrant, the calculated theoretical endpoint value, and a pH meter to determine the acid. Relative precisions of this method are in the range of 1 to 2 percent. This method combines the speed of the indicator method with the precision of the titration curve method.

EXPERIMENTAL PROCEDURE

Strict analytical chemistry methods and procedures are followed throughout this experimental procedure section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 2).

Two analytical reagent grade standard solutions are required. The first solution is a 40 ± 0.01-g/l sodium hydroxide solution that is standardized with primary standard potassium acid phthalate as outlined in References 2 and 4. The second is a 7 ± 0.05-pH unit standard buffer solution. This buffer solution is standardized against the primary standard buffer solutions in Table 11-1 of Reference 3.

Preparation of either an anodizing or hardcoating sample solution for titration analysis requires that 10 milliliters (ml) of the sample solution is pipetted into a 400-ml beaker. The beaker is then filled to approximately the 200-ml mark with deionized water and a stirring bar is added.

Calibration of the pH meter is accomplished using the pH = 7 buffer solution. The pH readings for the buffer solution may not vary by more than 0.10 pH unit.

The sulfuric acid sample solutions are titrated using sodium hydroxide titrant to an endpoint at 7 ± 0.10 pH units recording the amount of titrant dispensed in milliliters at the endpoint as "reading A."

All standard and sample solutions are analyzed in triplicate. Sulfuric acid concentrations in the samples are calculated by normal chemical stoichiometry.

RESULTS AND DISCUSSION

Experimental acid-base titration data are presented in Table I for sample anodizing solutions one and two and in Table II for sample hardcoating solutions three and four. The acid-base titration consists of the following two equations to various definite extents:

$$H_2SO_4 + NaOH \text{ <--> } NaHSO_4 + H_2O \quad (1)$$

$$NaHSO_4 + NaOH \text{ <--> } Na_2SO_4 + H_2O \quad (2)$$

The calculation for determining the concentration of sulfuric acid in the sample solutions is

$$g/l\ H_2SO_4 = (A)\ (B)\ (9.8) \quad (3)$$

where

A = "reading A" in ml

B = titrant normality

and the constant value in Eq. (3) is the combined result of many constants (ref 2).

Using Eq. (3), the respective sulfuric acid values for sample solutions one and two in Table I are 95.4 and 144.3 g/l. Likewise, using the same equation, the respective sulfuric acid values for sample solutions three and four in Table II are 124.4 and 143.6 g/l.

It is useful to evaluate the variations in precision for the materials and methods used. Tables III through VII present the data for the 10-ml class-A pipets, pH = 7 buffer solution, pH meter reading at pH = 7, 40-g/l sodium hydroxide titrant, and 50-ml class-A burets, respectively.

The data obtained by this method are sufficient to adequately monitor the sulfuric acid in the anodizing and hardcoating aluminum finishing processes, thus providing efficient use of resources. The optimum operating ranges of this acid are 90 to 150 g/l and 120 to 150 g/l for the respective anodizing and hard-coating solutions. The resulting precisions are in the range of 1 to 3 g/l, providing adequate monitoring of these metal finishing solutions supported by seven years of testing.

REFERENCES

1. Metal Finishing Guidebook, Metals and Plastics Publications, Inc., Hackensack, NJ, 1984.

2. J. Fritz and G. Schenk, Quantitative Analytical Chemistry, Fifth Edition, Allyn and Bacon, Inc., Boston, MA, 1987.

3. D. Peters, J. Hayes, and G. Hieftje, Chemical Separations and Measurements: Theory and Practice of Analytical Chemistry, W. B. Saunders Company, Philadelphia, PA, 1974.

4. R. Brumblay, Quantitative Analysis, Harper and Row Publishers, New York, 1972.

TABLE I. EXPERIMENTAL TITRATION DATA FOR ANODIZING SAMPLE SOLUTIONS ONE AND TWO

Replicates	Sample One Titrant Used (ml)	Sample Two Titrant Used (ml)
1	9.75	14.70
2	9.75	14.80
3	9.75	14.75
X(avg)	9.75	14.75

TABLE II. EXPERIMENTAL TITRATION DATA FOR HARDCOATING SAMPLE SOLUTIONS THREE AND FOUR

Replicates	Sample Three Titrant Used (ml)	Sample Four Titrant Used (ml)
1	12.70	14.65
2	12.75	14.70
3	12.70	14.70
X(avg)	12.72	14.68

TABLE III. PRECISION OF A 10-ml CLASS-A PIPET

Replicate	10-ml Pipet Volume (ml)*
1	10.02
2	10.00
3	10.02
4	9.98
5	9.98
6	9.98
X(avg)	10.00
Sn	0.02

*Volumes are calculated from the weight-volume relationship of a pipetted deionized water solution corrected for temperature.

TABLE IV. PRECISION OF A pH = 7 BUFFER SOLUTION

Replicate	pH = 7 Buffer Solution*
1	7.05
2	7.02
3	6.98
4	6.99
5	6.95
6	6.95
X(avg)	6.99
Sn	0.04

*The pH values are standardized against primary standard buffer solutions in the potentiometry chapter of Reference 3 using a pH meter.

TABLE V. PRECISION OF READINGS AT pH = 7

Replicate	pH = 7 Readings *
1	7.02
2	7.03
3	7.01
4	6.99
5	6.98
6	7.02
X(avg)	7.01
Sn	0.02

*The pH values are standardized against primary standard buffer solutions in the potentiometry chapter of Reference 3 using a pH meter.

TABLE VI. PRECISION OF A 40-g/l SODIUM HYDROXIDE STANDARD SOLUTION

Replicate	Sodium Hydroxide (g/l)*
1	40.01
2	40.00
3	39.99
4	39.99
5	40.01
6	40.00
X(avg)	40.00
Sn	0.01

*Sodium hydroxide concentrations are calculated by titration using the primary standard potassium acid phthalate for standardization.

TABLE VII. PRECISION OF A 50-ml CLASS-A BURET

Replicate	Volume (ml)*
1	24.94
2	24.98
3	25.02
4	25.05
5	24.98
6	25.05
X(avg)	25.00
Sn	0.04

*Volumes are calculated from the weight-volume relationship of a contained deionized water solution corrected for temperature at a point one-half full--25 ml.

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